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A NEW METHOD FOR THE FABRICATION OF POLYCRYSTALLINE HYDROGEN-CONDUCTING SOLID ELECTROLYTES

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A NEW METHOD FOR THE FABRICATION OF POLYCRYSTALLINE HYDROGEN-CONDUCTING SOLID ELECTROLYTES

by

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ABSTRACT

This report describes the synthesis and fabrication of polycrystalline ceramic materials that conduct electricity by the mobility of hydrogen ions or hydronium ions and are stable to temperatures above 100°C.

The process avoids the usual sintering of a polycrystalline precursor and its subsequent ion-exchange to the hydronium form with the attendant micro-cracking and drastic decrease in strength. Instead, the precursor powder is first transformed to the hydronium form and this is bonded under pressure at temperatures less than 200°C using appropriate mineral phosphates to produce dense, strong bodies of high conductivity.

This process is simple and quick and does not require significant capital investment. It is presently the subject of a patent application arising from the development work conducted under the Project: 3.0.2.9.02 "Hydrogen-Air Fuel Cell".

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NOUVELLE MÉTHODE UTILISÉE POUR LA PRODUCTION D'ÉLECTROLYTES SOLIDES POLYCRISTALLINS CONDUCTEURS D'HYDROGÈNE

par

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RÉSUMÉ

Le rapport présente une description des procédés de synthèse et de fabrication de produits céramiques polycristallins qui, en raison de la mobilité des ions d'hydrogène ou des ions d'hydronium, sont conducteurs d'électricité et demeurent stables jusqu'à des températures supérieures à 100°C.

Le procédé permet d'éviter le frittage du précurseur polycristallin qui se produit habituellement et sa transformation en hydronium lors de l'échange d'ions subséquent ainsi que le microcraquage et la diminution radicale de résistance qui s'ensuivent. Au lieu de cela, la poudre dérivée du précurseur est, dans un premier temps, transformée en hydronium et ce produit est aggloméré sous pression à des températures inférieures à 200°C au moyen de minerais phosphatés appropriés afin de produire des corps denses et concentrés à haute conductivité électrique.

Ce procédé est simple et rapide et n'exige pas des investissements en capital importants. Le procédé fait actuellement l'objet d'une demande de brevet d'invention à la suite des travaux de développement effectués dans le cadre du projet: 3.0.2.9.02 "Pile à combustible hydrogène-air".

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INTRODUCTION

The opportunity to ion-exchange many materials is well known and gives rise to wide range of products, be they based on organic resins or inorganic materials such as clays. It was recognized early in the development of solid electrolytes that the same opportunity might exist for cationic conductors, hence from the early 1970's more and more academic enquiry was directed along these lines. In general, provided that charge compensation can be achieved, a number of cationic analogues can be produced using various anionic lattices as hosts.

With the academic and commercial interest to develop these materials for either sensors or energy systems (batteries, fuel cells, thermoelectric generators, etc.) there has been keen interest in examining the highly conducting host lattices and producing a range of materials conductive to one ion or another. This opportunity to ion-exchange a variety of anionic lattices that may be one-, two- or three-dimensional conductors gives a wide range of possibilities.

Following the sharp rise in the world price of oil in 1973, there was a flurry of R&D activity in developing materials conductive to lithium and sodium suitable for use in battery systems. This stimulated the work already in progress on the highly conductive sodium beta-aluminas (a non stoichiometric sodium aluminate) and later (1976) with the so-called zirpsios (a solid solution series of sodium zirconium phospho-silicates). Towards the end of the 1970's, this interest extended to examining the production of the hydrogen conducting forms. Not only was it found that such forms exist but, in the case of beta"-alumina and the zirpsios, that the conductivity can be better than 10^{-5} $(ohm.cm)^{-1}$ at 100°C. However, the products in every case were powders or single crystals and clearly unsuitable for use as the extensive high-surface-area electrolyte membrane required for fuel cells.

A recent review by the authors of hydrogen-conducting solids shows that high conductivity can occur by either a vehicle mechanism or a hopping mechanism (a third mechanism, proton tunneling, is assumed to occur in dehydrated materials and results in very low conductivity) (1). The vehicle mechanism assumes that an itinerant proton attaches itself to a water molecule forming the hydronium ion (H_3O^+), which moves through the lattice

in the conduction plane while water moves in the opposite direction. This mechanism is in contrast to the Grotthus or hopping mechanism in which the host H_2O remains immobile and the proton moves from one molecule to another as they rotate and move into a favorable configuration. The vehicle mechanism has been suggested to operate in the hydronium and ammonium beta-aluminas and the hopping mechanism in hydrogen uranyl phosphate, $H_2Sb_4O_{11}$ and others. Clearly, the Grotthus hopping mechanism would be favoured when there is a high concentration of nucleophilic groups that can rotate readily, passing the proton from one to another, whereas the vehicle mechanism would be favoured when there is nearly an equal concentration of ions and vacant sites.

The implications of these two principal conduction mechanisms are that the materials must be a hydrate to conduct well and that it must retain this water to the anticipated operating temperature of any device. Unfortunately, may of the known room-temperature proton conductors are unstable on heating and can suffer a decrease in conductivity of three or more decades between 25° and 50°C (1). Although many materials exhibit a protonic conductivity that is very temperature dependent, the initial work conducted during the 1970's did identify the beta-alumina and zirpsio lattices as having high conductivity at temperatures above 100°C. Differential thermal analysis of single crystal beta-alumina, in particular, suggests that it loses reversible water at about 260°C and the remaining irreversible water at 400°C, indicating it is an ideal candidate material for exploitation in a fuel cell and a steam electrolyser.

PRODUCTION OF HYDRONIUM ION CONDUCTING POLYCRYSTALLINE CERAMICS

MATERIALS LIMITATIONS

The general principle by which such materials are produced is to acid exchange the alkali-ion form and thereby produce the H_3O^+ analogue. However, there are several aspects of the real systems that force the materials designer to some unusual processes if any polycrystalline sheets or tubes of these materials are to be produced. For example, the replacement of the smaller Li- or Na-ions (ionic radii: Li^+ = 0.065, Na^+ = 0.096 nm) by the much bigger hydronium ions (ionic radius = 0.148 nm) by the

direct exchange of a sintered polycrystalline body in weak acid results in a considerable lattice expansion and the shattering of the body.

On the basis of ionic radius alone, it would appear useful to exchange the K^+-ion form (ionic radius K^+ = 0.135 nm) as this would minimize the induced strain. However, for the materials showing reasonable high-temperature stability and therefore of interest in the CANMET program, the zirpsios do not retain the anionic lattice structure needed for high conductivity when the K-form is synthesized directly (2) and the meta-stable nature of the K beta"-alumina system only allows the formation of the beta-phase on high-temperature sintering and this is an insulating phase after ion exchange to the hydronium form (10^{-11} $(ohm.cm)^{-1}$) at room temperature) (1).

This behaviour of both materials as sintered polycrystalline bodies is in contrast to their behaviour as powders or single crystals. In both cases, as powders, it is possible to form a highly conductive phase if the Na^+-form is first synthesized and then transformed to a highly conducting hydronium powder by refluxing in acid. Unfortunately, the hydronium form cannot then be sintered without dehydrating and collapsing the anion lattice, thereby destroying all conductivity. Therefore, the challenge for the materials scientists was to develop in the sintered body the characteristics that had been observed in the single crystal form. Clearly this demanded that the lattice be dilated prior to or during the sintering process so that exchange to the final hydronium form does not shatter the body.

EXISTING PROCESSES

Two principal routes have been followed to achieve this end and both depend on the incorporation of potassium into the lattice prior to the final exchange to the hydronium form. In one case, the sintered Na-form is converted to the K-form by exchange in potassium vapour at 1400°C in all-platinum equipment followed by refluxing in acid to form the hydronium form (3). Provided the exchange occurs at these elevated temperatures, the lattice is sufficiently annealed so that fracture does not occur. An alternative route is to incorporate potassium into the nominally sodium composition prior to calcination thereby ensuring that a dilated lattice is created directly the final phase is formed. The sintering of this material

is followed by an ion-exchange of some of the remaining sodium using either a molten potassium chloride or nitrate salt bath followed by a final ion exchange to the hydronium form using a field-assisted ion exchange (FAIE) technique in dilute acid at about 90°C (4-6). Yasicon and Gasicon hydronium ion conductors are also claimed to be prepared by a similar process (7).

The existing procedures are multi-stage processes that are difficult and time consuming and often the products tend to crack resulting in a low yield. In those cases where the materials are not macrocracked, they are always badly microcracked and this results in low strength, which is undesirable for some of the intended applications. Also, in the FAIE stage, only a partial exchange of the sodium and potassium ions by the hydronium ions can be allowed or else the material develops cracks during extended ion exchange. Another requirement in the sinter process is to retain a high proportion (>60%) of the beta"-phase in the sintered sodium/potassium material in order to have high ionic conductivity after hydronium ion exchange. This is very difficult to achieve and requires very stringent control of the powder preparation, calcination and sintering stages.

German patents (8,9) claim that sodium zirpsios (Nazirpsios) can be converted into hydronium forms by direct ion exchange of the sodium ions in acids. However, our own experience with sintered polycrystalline Nazirpsios shows that if they are treated with hot acids so that the exchange is substantially complete the bodies shatter into small pieces. Presumably, the hydronium conductivity that is claimed is achieved by a very limited exchange, perhaps less than 10% of that possible, so that cracking is avoided. However, such materials, although suitable for potentiometric applications in sensors, are quite unsuitable in any device that must handle significant power loads (fuel cell or electrolyser) as there will be too low a concentration of carriers for sensible performance. There is also a further difficulty of using only partially exchanged material in a polarized device: the remaining mobile sodium ions will migrate to the cathode side, deposit as the metal and form an interfacial layer of hydroxide and perhaps bicarbonate (if exposed to air) between the electrolyte and the electrode layer. This will result in the electrode peeling from the surface and will increase the concentration polarization and probably the activation polarization in that half-cell.

Unfortunately, the stability of hydronium-containing beta/beta"-alumina materials is poor above about 500°C, rendering impossible the formation of cohesive bodies by any form of high temperature sintering process. Consequently, it has proved impossible to produce a fully exchanged polycrystalline hydronium body having high strength; the best achieved so far is the partial exchange of a sintered mixed ion Na/K conductor of a two phase beta/beta"-alumina produced by McMaster University under contract to the Division of Energy, NRC. However, such products have been shown by ultrasonic non-destructive testing to be heavily microcracked even prior to use and to be extremely fragile (10).

This is in sharp contrast to the characteristics of the CANMET-produced materials, which are essentially fully exchanged, exhibit high conductivity and mechanical strength, and can be produced in a fraction of the time it takes to produce materials using the existing processes. Furthermore, it is not essential to use freeze-dried precursor powders as is required elsewhere and the moulding process does not require special capital equipment.

THE NEW APPROACH

In contrast to existing processes that attempt to dilate the lattice of a sintered body without micro- or macro-cracking prior to forming the hydronium form, the CANMET process does not depend on sintering and also avoids the need to dilate the lattice prior to creating the hydronium conductor.

The essence of the CANMET-developed process is just the opposite of the earlier processes. First, the precursor materials are ion exchanged while still in powder form so that the expansion that occurs is not restrained and hence is of no consequence. Thereafter, the powder is directly bonded using a second phase of either an aluminum or zirconium phosphate, which themselves are moderately good hydronium conductors. Provided the concentration of this added material is low, i.e., the grain boundary thickness is kept small, the product retains its high conductivity and also exhibits a much higher strength than the materials produced by other processes.

In the new process, precursor powders produced by spray drying, freeze drying or any other process can be used. The precursor powders are calcined and the products are boiled with an acidic solution to create hydronium ion conducting solid electrolyte powders. These powders are then bonded by the

incorporation of phosphoric acid into the materials to form a plastic body that is then pressed to shape, followed by curing. Fully exchanged hydronium ion conducting beta"-alumina (free of the insulating beta-alumina phase) and zirpsios have been successfully fabricated by the new technique.

EXPERIMENTAL PROCEDURES AND RESULTS

CONVERSION OF SODIUM- TO HYDRONIUM-ION CONDUCTING CRYSTALLINE POWDERS

(i) Hydronium beta/beta"-alumina

A sample of sodium beta/beta"-alumina precursor powder is prepared by any known method (11). The powder is calcined at a temperature ranging between 1300° and 1700°C in order to form and crystallize the sodium beta/beta"-alumina. A known mass of the powder is placed in a round bottom flask and refluxed with a calculated amount of 0.1N aqueous solution of hydrochloric or sulphuric acid for 4-12 h. (The longer times are used for samples containing larger crystals that are prepared by calcination at the high temperatures.) Ion exchange of the sodium by hydronium takes place during this operation. The progress of the ion exchange is monitored by analysing the extract for sodium content by atomic adsorption. A pH of <3 is maintained in the solution during the ion exchange. When the exchange is complete, the mixture is allowed to cool and the precipitate of hydronium beta/beta"-alumina is filtered and washed with distilled water free of sodium ions and dried in an air oven at about 90°C.

Partial X-ray diffraction charts of the beta/beta"-alumina before and after hydronium ion exchange are shown in Fig. 1. It is clear that the crystallinity of the material is intact after the exchange although there are some changes in the d-spacings. These changes are due to the expansion of the crystal lattice of the beta/beta"-alumina when the sodium ions are displaced by the larger hydronium ions.

An X-ray diffraction pattern of the hydronium beta/beta"-alumina after it is heated at 800°C is presented in Fig. 2. No beta/beta"-alumina is present in the material after the high temperature heat treatment. This is because of the total decomposition of the hydronium beta/beta"-alumina at that temperature. If the material contained any sodium beta/beta"-alumina

then the X-ray diffraction pattern would have shown its presence because sodium beta/beta"-alumina is stable even at temperatures greater than 1600°C. This proves that the hydronium ion exchange of the sodium form was complete under the hot dilute acid conditions used for the exchange.

In Fig. 3 are given scanning electron micrographs of the powders before and after hydronium ion exchange of the sodium beta/beta"-alumina. During ion exchange, the single crystal aggregates of the sodium beta/beta"-alumina get separated more into single crystals and the crystals themselves retain their shape remarkably after exchange. An EDAX microanalysis of the ion exchanged crystals showed no detectable amounts of sodium in them. This again proves the displacement of the sodium by hydronium ions in the ion exchange process.

Results of a thermogravimetric analysis of the hydronium beta/beta"-alumina powder are presented in Fig. 4. The sample begins to lose weight at about 100°C and the weight loss continues to increase with increase in temperature up to about 800°C. There is an increase in the rate of weight loss beginning at 200° with a maximum rate at about 300°C. Approximately 70% of the total weight loss occurs by 400°C. It is assumed that water is being lost from the hydronium beta/beta"-alumina during heating over 100°C.

(ii) Hydronium Zirpsios

A sodium zirpsio precursor (Hong x = 1.5) powder is prepared by the sol-gel technique (12,13) or any other method. The powder is then calcined at 1200°-1300°C to form a soft cake of Nazirpsio microcrystals. The crystalline powder thus obtained is refluxed with 0.1N hydrochloric acid as above to convert the sodium zirpsio into hydronium zirpsio. The product is washed thoroughly with distilled water and dried at about 90°C.

X-ray diffraction charts of the sodium and hydronium zirpsios are presented in Fig. 5. After exchange, the product retains its crystallinity, but the diffraction patter is considerably different. This is the result of the displacement of the sodium by the considerably larger hydronium ion. An X-ray diffraction pattern of the hydronium zirpsio after calcination at 800°C is shown in Fig. 6. The zirpsio pattern has been totally destroyed, showing that the product was completely ion exchanged with the acid treatment.

Results of thermogravimetric analysis of the hydronium zirpsio are shown in Fig. 7. The decomposition starts at around 120°C and goes through a fast reaction up to about 200°C, but no further decomposition occurs until about 300°C when another reaction sets in, the majority of which is complete by 425°C. The decomposition is complete at 800°C. The total weight loss amounts to about 7% and the initial loss (120-300°C) is less than 30% of this.

SEM micrographs of the zirpsio before and after hydronium ion exchange are displayed in Fig. 8. The Nazirpsio powder consists of crystal aggregates, but the hydronium form contains more single crystals. In spite of the expansion and contraction of the crystal lattice during the hydronium ion exchange, the crystals themselves have not disintegrated.

An EDAX analysis shows that the hydronium zirpsio contains about 10% of the amount of sodium present in the sodium form. If only the mobile sodium ions are displaced by the hydronium ions during exchange, then about 40% of the sodium would have been present in the product. This indicates that the acid treatment removes much more than the normally mobile sodium ions in the Nazirpsio without destroying the crystal structure.

The same process has been found to be applicable to zirpsios with any value of x in the range from 1.5 to 2.4.

BONDING OF THE HYDRONIUM-ION SOLID ELECTROLYTES

The crystalline powders of hydronium ion conducting solid electrolytes prepared as described above are bonded into discs or other shapes by the incorporation of orthophosphoric acid to the powder and curing the resulting product.

In one procedure, 1.5 g of the hydronium beta/beta"-alumina were ground with 0.6 g of orthophosphoric acid in an agate mortar and the resulting mixture was pressed in a 2.5 cm diameter steel die with Teflon lining and Teflon caps at a pressure of about 14 KPa. The pellet was removed from the die and dried in an air oven at about 80°C for 3 h. It formed a hard disc of density 2.8 g/mL measured from the physical dimensions.

In another procedure, the mixture prepared as above was pressed in a Teflon lined die and heated under pressure at about 14 KPa and 120°C for 30 min. A hard disc of density 3.08 was obtained. The procedure described

above for the hydronium beta/beta"-alumina applies to the hydronium zirpsios also; hard discs of density about 2.6 g/mL are obtained.

In the case of hydronium beta/beta"-alumina, it is desirable to use orthophospnoric acid containing distilled water (e.g., 80% solution) to make the bonding mixture. Although the incorporation of water reduces the final density of the bonded product, it improves its thermal stability beyond 100°C. The product made with 100% phosphoric acid tends to bloat and crack when heated to temperatures above 100°C. Samples made with 80% phosphoric acid have been heat-treated to 300°C without any signs of bloating or cracking. The effect of the strength of the acid used for the bonding on the density of the bonded beta/beta"-alumina is illustrated in Table 1.

The mechanism of bonding of the hydronium beta/beta"-alumina is believed to be the formation of aluminum and magnesium acid phosphate by the interaction of the phosphoric acid with part of the material and the resulting hard-setting of the phosphates. Because the acid phosphates are generally protonic conductors, in the bonded product the hydronium beta/beta"-alumina crystals are bridged by a protonically conducting matrix resulting in overall high protonic conductivity in the composite. The reason for the instability of the product made with 100% phosphoric acid may be the formation of highly unstable aluminum phosphate-phosphoric acid complexes such as $AlPO_4.2H_3PO_4$. The presence of water avoids the production of this phase because it is decomposed by water. Thermogravimetric analyses of the phosphate-bonded hydronium beta/beta"-alumina made respectively with the incorporation of 100% and 80% aqueous phosphoric acid are given in Fig. 9. A large weight loss occurs in the product from 100% phosphoric acid, amounting to about 11% by weight to about 250°C, which explains the bloating and cracking behaviour of these discs. On the other hand, the discs made using 80% phosphoric acid have a much smaller weight loss (7.5%), which makes them relatively more stable when heated. In Fig. 10 are shown photographs of discs of phosphate-bonded hydronium beta/beta"-alumina made with 80% phosphoric acid before and after heating to 300°C. No cracking or breakdown of the disc is apparent.

An X-ray diffraction analysis of the bonded beta"-alumina (Fig. 11a) showed that the material essentially consisted of hydronium beta/beta"-alumina. The small extraneous peaks represent various forms of aluminum phosphate.

In the case of the hydronium zirpsios, the interaction with phosphoric acid seems to produce zirconium acid phosphates that appear to be more stable than their aluminum counterparts. Zirconium phosphates are known to be protonic conductors (14). Discs of hydronium zirpsio (Hong x = 1.5) bonded using 100% phosphoric acid did not break down after heating to 300°C. A partial XRD chart of bonded hydronium zirpsio (x = 1.5) is shown in Fig. 11b. In addition to hydronium zirpsio, zirconium phosphates are present in the material. However, because the latter are hydronium conductors it is not expected to be detrimental.

A scanning electron micrograph of a polisned section of the bonded hydronium beta"-alumina (Fig. 12) shows that the crystals have been partially reacted by the phosphoric acid on the surface, thereby removing the sharp crystal boundaries that are present in the unbonded material. Because of the fineness of the microstructure, it is not possible to distinguish between the hydronium conducting crystals and the bonding materials by microprobe analysis.

CONDUCTIVITY OF THE BONDED PRODUCTS

Some preliminary studies on the ionic conductivities of the bonded hydronium beta/beta"-alumina and the hydronium zirpsio were carried out by the high frequency ac technique using a microprocessor controlled Solartron frequency response analyser system (15). The measurements were made in stagnant air using silver ink electrodes as contacts.

Typical data obtained at room temperature are shown in Fig. 13. Specific conductivities in the range of 10^{-5} to 10^{-2} $(ohm.cm)^{-1}$ at 100-120°C were obtained. Preliminary examination of the variation of conductivity with temperature suggests an activation energy of 5.8 kCal/mole over the range 25° to 120°C for the zirpsio-based products, whereas values obtained for the beta"-alumina-based materials ranged between 12 and 14 kCal/mole. These values are quite satisfactory for several devices using hydronium ion conducting solid electrolytes.

In view of the satisfactory strength and electrical conductivity, work has also been undertaken to exploit these materials in a simple hydrogen sensor and also in a hydrogen ion pump. The general experimental details have been given elsewhere (16).

Preliminary data were obtained from a zirpsio-based cell using Pt-Pt electrodes applied as a paste.

Figure 14(a) shows the response of the system to changes in the partial pressure of hydrogen and confirms that the system voltage responds directly to changes in hydrogen concentration. However, although the data do not coincide with those predicted using the Nernst equation, they do indicate that the material is responding reproducibly to the changes imposed. The deviation from the theoretical emf values is probably due to experimental anomolies such as leakage around the cell, poor gas mixing or the diffusion of silver into the electrolyte from the silver epoxy used to attach leads to the Pt electrodes.

The response of the system to an applied voltage, under which conditions the cell is acting as a hydrogen pump, is shown in Fig. 14(b). The current density J was deliberately kept low in this case. Other experiments with higher applied voltages have demonstrated that values of J up to 100 mA/cm^2 may be realistic for the use of these materials in high-temperature electrolysis systems.

SUMMARY

Hydronium ion conducting beta/beta"-alumina and zirpsios in powder form can be prepared by the direct exchange of sodium ions from their sodium analogues in hot dilute acidic solutions. A product containing 100% of the highly conducting hydronium beta"-alumina phase can be prepared by this route. Zirpsios in which about 90% of the sodium ions are displaced by hydronium ions also can be synthesized by the same technique. The materials do not break down during exchange, as shown by X-ray and SEM analyses.

The hydronium conductor powders can be bonded into strong bodies by mixing them with phosphoric acid and forming them into the required shapes for use in devices. The ionic conductance of the bonded products has been in the acceptable range for several applications.

A simple process has thus been developed for the fabrication of hydronium ion conducting ceramic electrolytes without using the laborious steps required by prior techniques described by others.

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TABLE 1.

The Effect of the Strength of Phosphoric Acid on the Density of Bonded Hydronium beta"-Alumina

Acid Strength %	Density of Disc g/mL
100	3.08
80	2.85
70	2.76
60	2.74
50	2.36
40	2.25
25	1.99

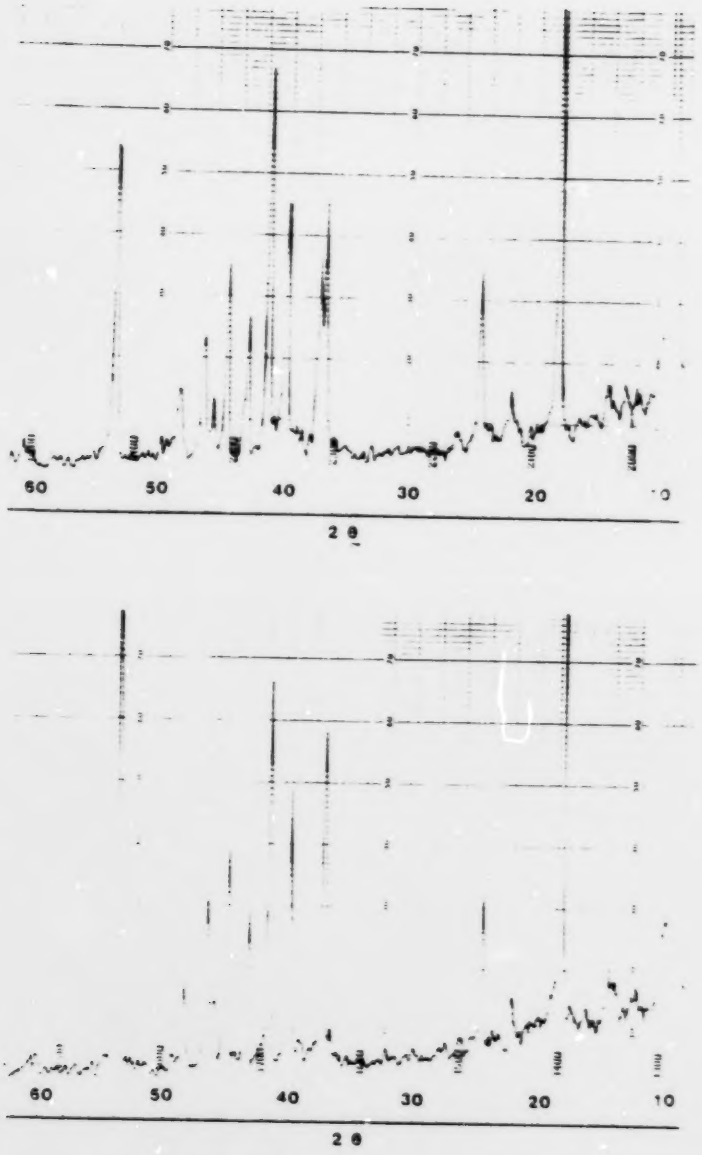

Fig. 1 - Partial X-ray diffraction patterns obtained on (a) sodium beta"-alumina and (b) hydronium beta"-alumina powders (Cu K-alpha).

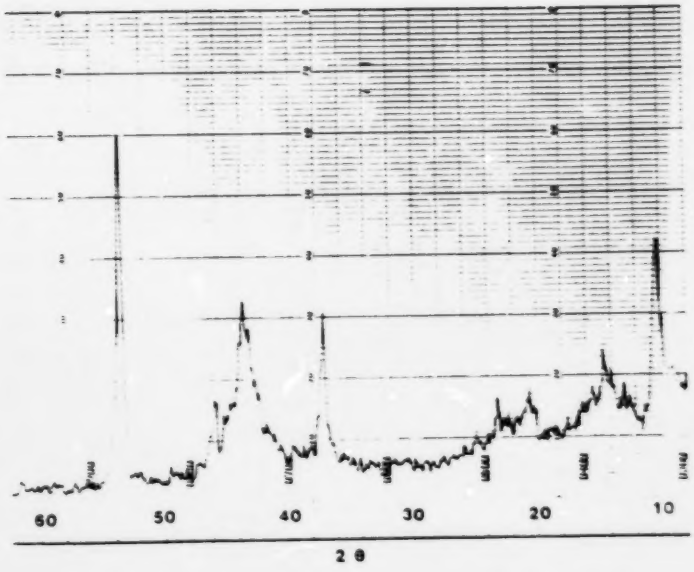

Fig. 1 - Partial X-ray diffraction pattern of hydronium beta"-alumina after heating to 600°C (Cu K-alpha).

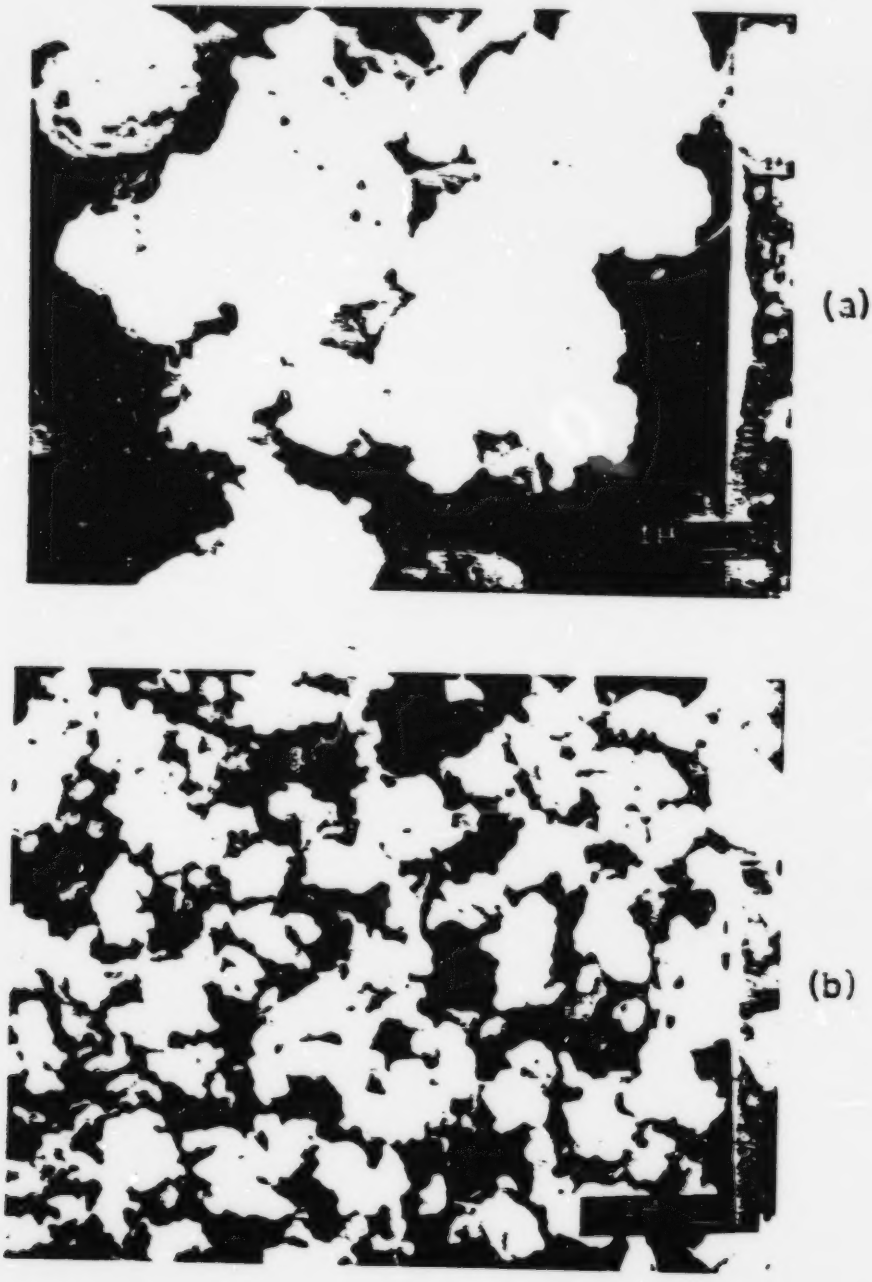

Fig. 3 - Scanning electron micrographs of Hong x = 1.5 compositions as (a) the sodium and (b) the hydronium form.

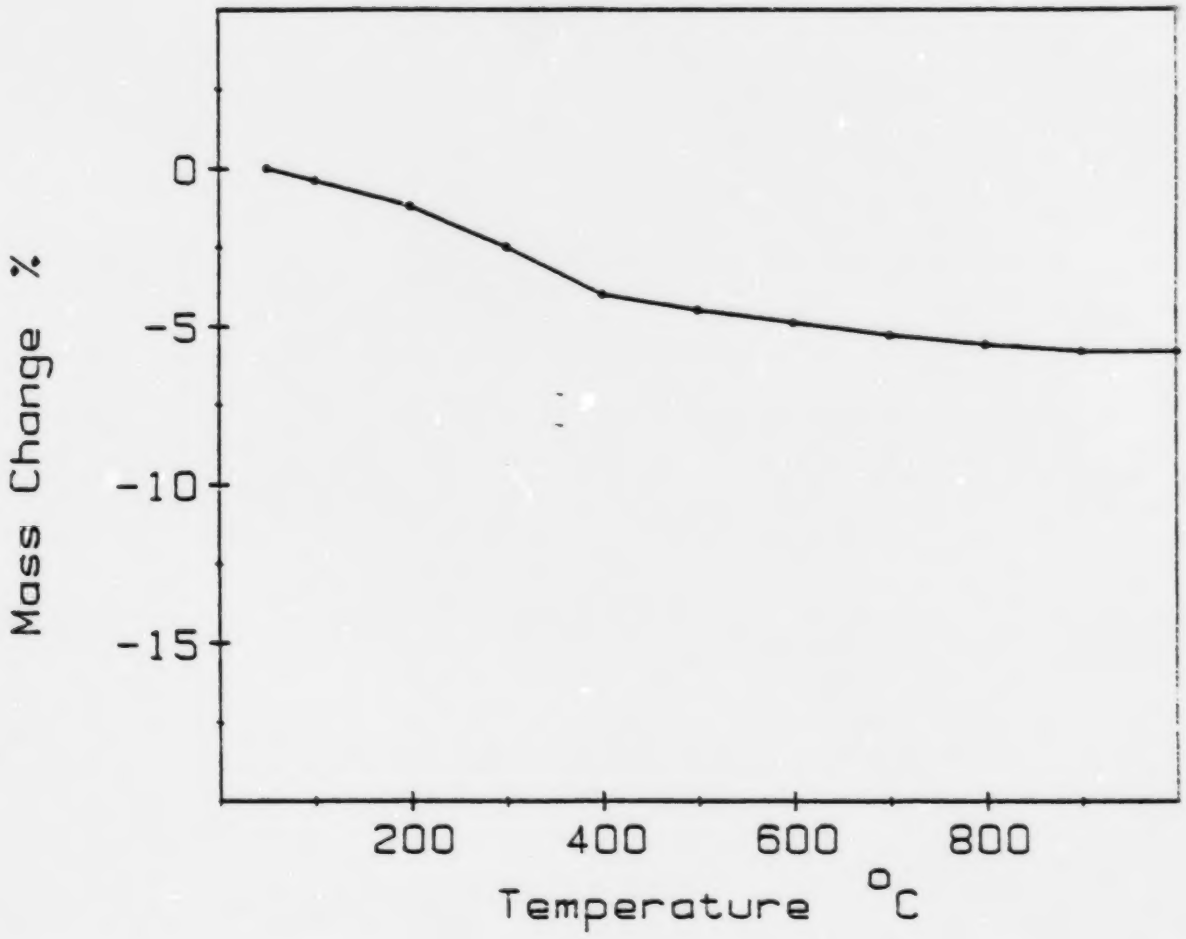

Fig. 4 - Thermogravimetric analysis of beta"-alumina powder heated at 10°C/min to 1000°C.

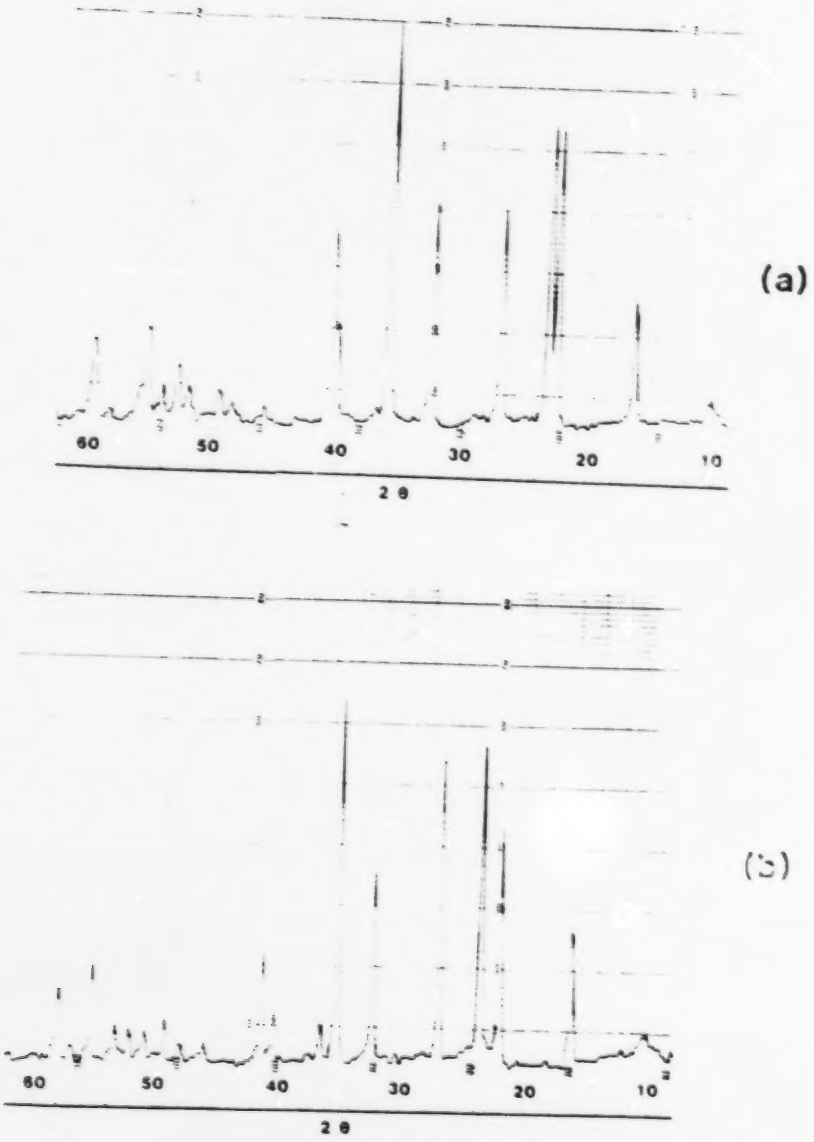

Fig. 5 - Partial X-ray diffraction patterns of (a) sodium form and (b) the hydronium form of the zirpsio powders shown in fig. 4 (Ω K-alpha).

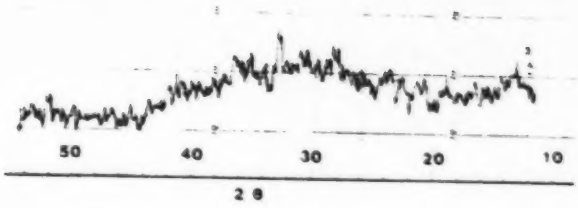

Fig. 6 - Partial X-ray diffraction pattern of hydronium zirpsio after heating to 800°C for 30 min.

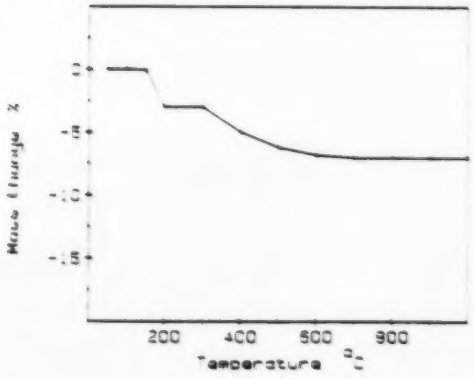

Fig. 7 - TGA of the decomposition of a Hong x = 1.5 hydronium zirpsio on heating to 1000°C.

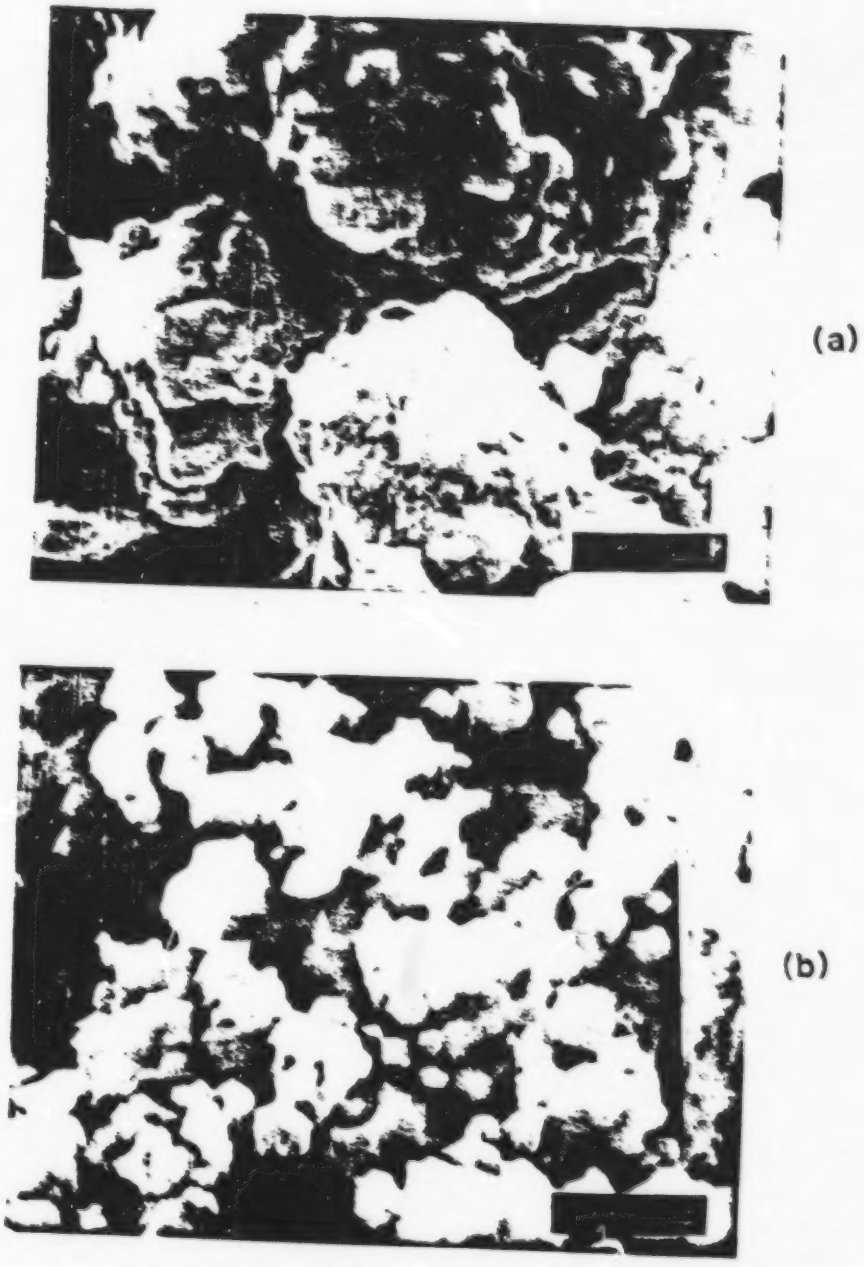

Fig. 8 - SEM Micrographs of (a) the sodium form and (b) the hydronium form of Hong x = 1.5 zirpsio powders.

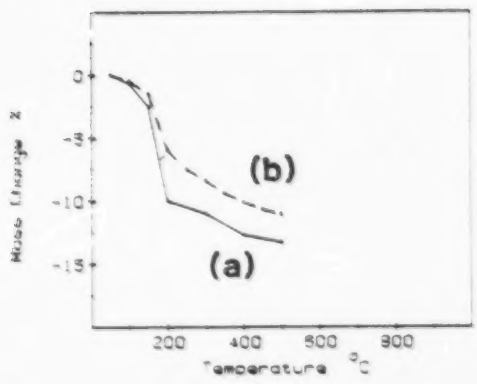

Fig. 9 - TGA of bonded hydronium beta"-alumina material produced using (a) 100% phosphoric acid and (b) 80% phosphoric acid.

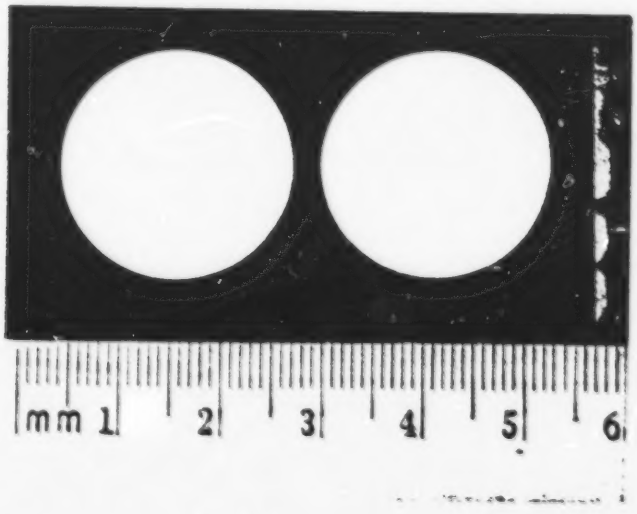

Fig. 10 - Samples of bonded hydronium beta"-alumina before (left) and after heating to 300°C in air.

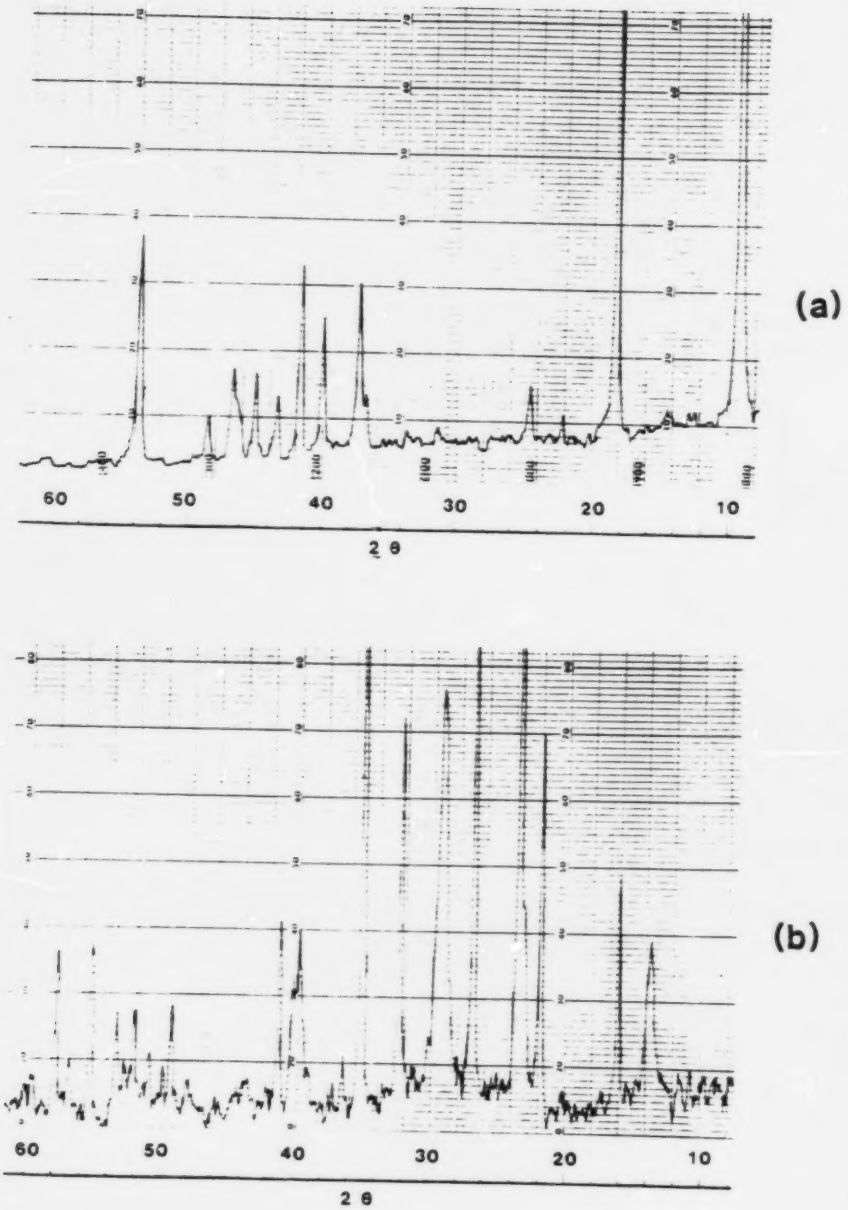

Fig. 11 - X-ray diffraction patterns of bonded hydronium material of (a) beta"-alumina and (b) Hong x = 1.5 zirpsio.

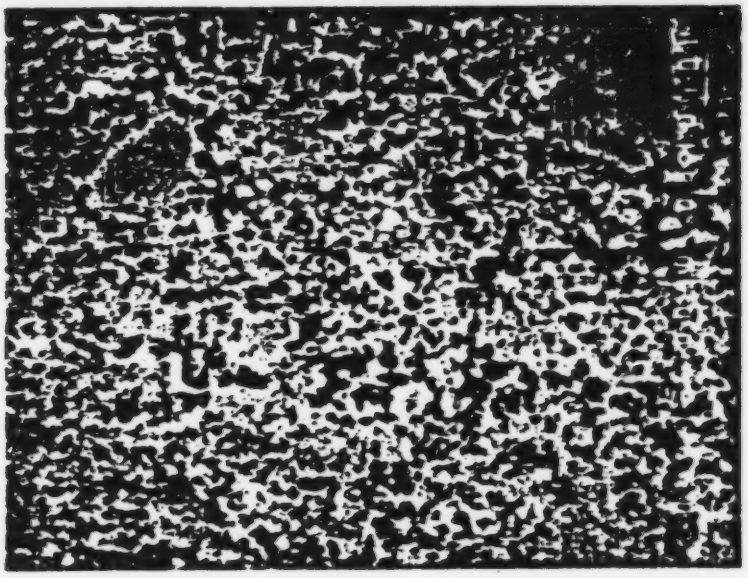

Fig. 12 - SEM of polished section of bonded beta"-alumina.

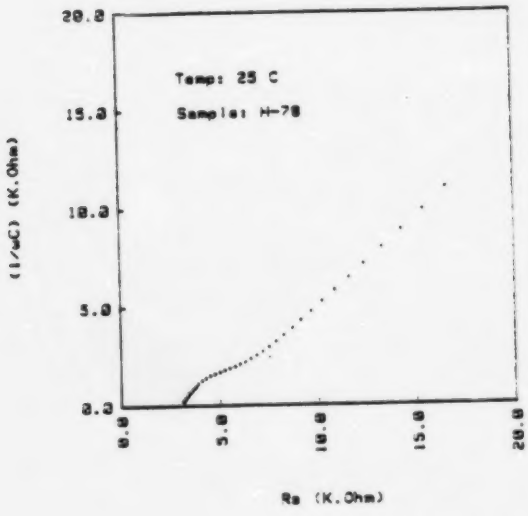

Fig. 13 - Impedance diagram obtained for bonded beta"-alumina obtained at 25°C using Pt electrodes.

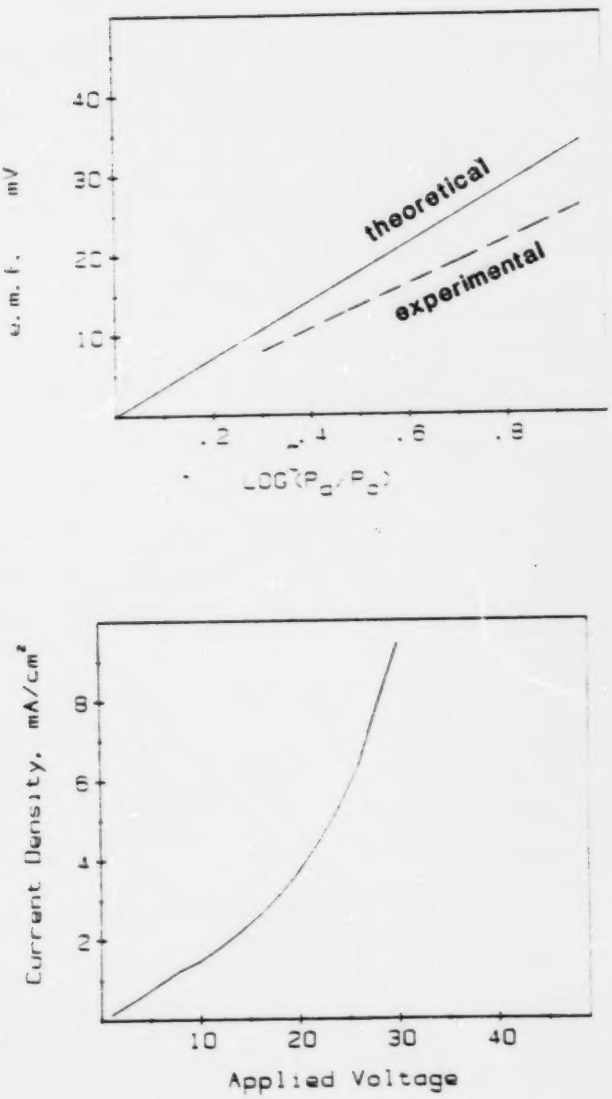

Fig. 14 - Behaviour of bonded hydronium zirpsio discs when used as (a) a hydrogen sensor and (b) a hydrogen pump.